Shock wave initiation of the Ti_5Si_3 reaction in elemental powders

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Elemental powder mixes were subjected to plane-wave shock processing which reduced the initial porosity to essentially zero. Two powder mixes in a 5:3 Ti:Si atomic ratio were used: −325 mesh Ti and Si (<45 μm), and −100 mesh Ti and Si (<150 μm) with shock pressures up to 7.3 GPa and shock energies up to 671 J/g. Shock pressures were calculated using hugoniot parameters for porous elemental powder mixtures and shock energies were taken to be the work done by the shock ($P\Delta V/2$). Shock energy thresholds for complete reaction of the elemental powders were found which depend upon powder particle size and the initial porosity of the powder. The threshold energy for the larger powder mix was found to be ~80% larger than that for the smaller powder. A decrease in initial porosity from 0.49 to 0.40 caused an increase in threshold shock energy of about 75% for both powders. At shock energies slightly below the threshold energy, evidence for the reaction of solid Ti and liquid Si was observed in small isolated regions. These regions contained spherical micronodules with the composition of $TiSi_2$ in Si. The results are compared to those of previous studies reported in the literature, and mechanisms for reaction initiation and the observed threshold values are proposed. © *1997 American Institute of Physics.* [S0021-8979(97)07017-5]

I. INTRODUCTION

This investigation was undertaken to explore the particle size and initial powder porosity effects on reactions of 5Ti +3Si powder mixtures forming Ti_5Si_3. Solid-state and solid-liquid state mechanisms, which have been proposed for initiation and propagation of reactions, are critically examined and discussed.

Boslough and Graham,[1] using optical temperature measurements, demonstrated that exothermic energy release can occur on a time scale of 100 ns in 2 μm powders of Al+Ni shocked to 14 GPa. This clearly indicates that significant reaction in fine powders can occur in times comparable to mechanical equilibration times. They also noted that reaction was inhibited by pressures in excess of 20 GPa.

Graham[2] proposed a mechanistic model based on configuration change, mixing, activation, and heating (CONMAH) for *solid-state* shock induced reactions. Subsequent work by Graham and co-workers demonstrated the importance of the initial porosity and the void configuration on reaction initiation.

Krueger *et al.*[3] found an energy threshold for shock wave initiation of the NiSi reaction in porous −325 mesh (<45 μm) Ni+Si powders. The threshold corresponded to the energy to initiate the reaction thermally in a differential scanning calorimetry (DSC) for a zero porosity Ni+Si mixture which had previously been consolidated by a shock wave with an energy just below the threshold energy. The thermal energy to initiate the reaction in a DSC was found to monotonically increase with an increase in porosity. Thus, no apparent ''shock activation'' was found in the Ni+Si system. Since the thermal energy and corresponding bulk temperature determines whether or not bulk reactions occur in Ni+Si it was concluded that the reaction kinetics are slower than the temperature kinetics of equilibration of the particles behind the shock front. Therefore, in these mixtures reactions proceed on a time scale greater than several microseconds when the particle size exceeds about 10 μm.

Krueger *et al.*[4] found the conditions for shock initiation of the Ti_5Si_3 reaction in 5Ti+3Si powders (−325 mesh) were sensitive to both the initial porosity and the residual O_2 gas in the pores. Powders evacuated, back filled with Ar and evacuated to 0.2 Torr, had a threshold energy approximately three times the energy for reaction of an evacuated powder with residual O_2. This result was attributed to the very large negative heats of formation of Ti oxides, ΔH_f, which could trigger the Ti_5Si_3 reaction in the shocked powder even with small concentrations of O_2. (TiO_2:$\Delta H_f = -944$ kJ/mol, Ti_3O_5:$\Delta H_f = -2460$ kJ/mol, and Ti_5Si_3:$\Delta H_f = -288.8$ kJ/mol.)

Dunbar *et al.*[5] studied the reactions in shock processed 5Ti+3Si powders (1–5 GPa pressures) with an initial pressure of 1 atm of air in the pores. Powder mixtures of three different morphologies were used, coarse, medium, and fine. They used PVDF piezoelectric polymer stress-rate gauges to record stress pulses in the mixture (47% initial porosity). The coarse morphology powder had a higher threshold for reaction than the medium morphology powder. The fine morphology powder (1–2 μm Ti and 10 μm Si) exhibited a higher than expected threshold which was attributed to agglomeration of the Ti which inhibited good mixing of Ti and Si particles. Large increases in wave speeds, at pressures greater than 1 GPa, were found and were attributed to expanded volume states (up to 20%) *produced by thermal expansion* from a strong exothermic transformation *in the solid state*. The volume change associated with the solid–to–solid transformation is −20.8%, which would require a thermal expansion of about 40% to produce the reported expanded volume. Thermal expansion will not exceed a few percent

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upon heating the solid powder mix to the melting point. We question that this observation indicates a solid-state bulk transformation in 10 μm or larger powders which occur on the time scale of mechanical equilibration.

Thadhani's review of chemical reactions in shocked powders[6] distinguishes between shock-induced reactions which occur on a sub-microsecond time scale and shock-assisted reactions which are initiated by the shock, but proceed to completion after the shock pressure is released. Evidence for solid-state reactions and possible evidence for the suppression of reaction under conditions which produce Si melting are discussed. Vecchio *et al.*[7,8] studied reactions in shocked Mo+Si and Nb+Si and proposed that the threshold shock energy which was observed produces a critical melt pool size of Si. Recovered samples show evidence of a liquid phase reaction forming ~2 μm spherical nodules of silicide which were injected into liquid Si. Myers *et al.*[8] proposed that the metal-Si interface grows from the dissolution of the metal into molten Si, producing the molten intermetallic, followed by spheroidization, solidification, and expulsion into the surrounding liquid silicon melt. Reaction rates could not be obtained from the observations, but their analysis shows that full reaction can occur in times comparable to the duration of a 1 μs shock pulse for a constant reaction rate of 25 m/s in 50 μm particles. These silicide reactions could therefore be classified as either shock-induced or shock-assisted depending on the actual rate of reaction.

Deevi and Thadhani[9] concluded that silicides formed in shocked 2Ni+Si and 5Ti+3Si powders by *solid-state* processes. Powders produced by grinding a compact shock consolidated below the threshold shock energy show an exotherm in differential thermal analysis (DTA) scans nearly 200 °C lower than the exotherms observed in the DTA for elemental powders. This was interpreted as evidence for *shock activation* of the powder. They observed that the silicide reaction in 5Ti+3Si powders occurs at shock energies which produce *bulk* temperatures in the elemental powders which are *less* than the melting point of Si, and therefore concluded that this is evidence for a *solid-state* process. These conclusions are re-examined in the light of the results from the present investigation.

Meyers *et al.*[10] demonstrated that the threshold energy for reactions forming Nb and Mo disilicides is lowered by intense, localized shear deformation. Following Yu *et al.*[11] and others, they consider the total energy, E_t, to be the shock energy plus a deformation energy *due to nonshock processes*. The shock energy is equated to the work done by the shock, given by $P(V_{00}-V)/2$, where P is the shock pressure, and V_{00} and V are the initial and shocked specific volumes, respectively. We note that the work done by the initial shock is *partitioned* into dilatational energy and shear energy, and this shear does not *add* additional energy (as does chemical reaction energy). However, subsequent shear deformation may initiate and influence the rate of chemical reaction.

II. EXPERIMENT

Two different powder mixes were used with different sized powders: 99.5% Ti (Cerac) with 99.5% Si (Aesar), both −325 mesh; and −100 mesh 99.5% Ti (Cerac) with 99.96% Si, −100+120 mesh (Cerac). The fine powder mix was blended in 1,1,2-trifluoroethane in a 5:3 atomic ratio and dried in vacuum. Coarse powders were blended dry in the same ratio. The shock experiments were conducted using propellant driven stainless steel flyer plates in a 35 mm smooth bore launch tube. The 5 mm flyer plate is carried by a nylon sabot and strikes the powder directly without striking the powder containment fixture (Fig. 1). The result of this target assembly is a well-controlled plane-wave geometry.[4] The powders were loaded into the cylindrical powder cavity of the target assembly, leveled, and pressed to the desired porosity. The pressed powder depth was nominally 16 mm for each experiment. The barrel and powder were evacuated and back filled with 1 atm of Ar, and then evacuated again to about 0.2 Torr. It should be noted that the maximum shock pressures attained in the powders occur throughout the majority of the powder volume, radial *release* waves propagate into the powder from the cylindrical powder cavity of the target assembly. The flyer plate and powder thickness are adjusted such that the shock wave in the powder is *unloaded* by the catch-up wave reflecting from the back of the flyer after traveling through the majority of the powder thickness but before it reaches the solid surface at the bottom of the powder cavity. The catch-up distance for each experiment is listed in Table I.

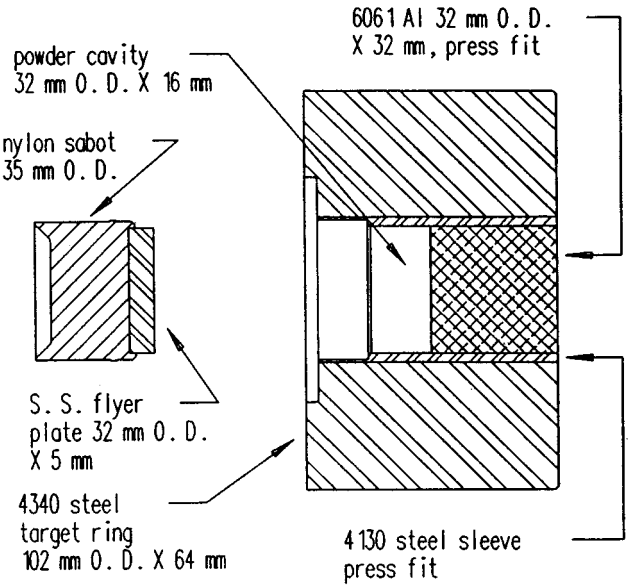


FIG. 1. Schematic drawing of the sabot with flyer plate and the target design.

The recovered compacts were sectioned by diamond sawing, mechanically polished, and examined optically, and by scanning electron microscopy (SEM) and x-ray diffraction (XRD).

III. EXPERIMENTAL RESULTS

Of the 15 shocked samples of the smaller powders, and the eight shocked samples of the larger powders, either fully reacted Ti_5Si_3 or fully consolidated compacts with little or no reaction were recovered as verified by XRD scans and opti-

TABLE I. Shock consolidation parameters.

Shot No.	Powder size	Porosity[a]	Impact velocity (m/s)	Shock energy (J/g)	Shock temp. (°C)	Shock press. (GPa)	Catch-up distance (mm)	Go/No go[b]
99	*S*	0.429	757	237	401	2.29	2.95	no
100	*S*	0.46	693	206	355	1.75	2.34	no
101	*S*	0.482	650	185	323	1.44	1.97	no
104	*S*	0.487	965	386	615	2.94	3.13	go
105	*S*	0.487	915	350	564	2.67	2.93	go
111	*S*	0.487	717	223	380	2.91	2.17	no
112	*S*	0.444	972	378	604	3.42	3.76	go
113	*S*	0.444	837	293	483	2.61	3.13	go
116	*S*	0.492	487	108	203	0.8	1.34	no
121	*S*	0.487	773	256	429	1.97	2.4	go
122	*S*	0.415	829	275	457	2.85	3.54	no
123	*S*	0.487	693	209	359	1.59	2.08	go
135	*S*	0.406	969	310	507	3.83	4.4	go
136	*S*	0.434	775	248	417	2.3	2.96	no
139	*S*	0.443	804	267	445	2.42	2.98	no
124	*L*	0.487	740	236	399	1.8	2.56	no
125	*L*	0.487	783	262	437	2	2.42	no
126	*L*	0.487	855	308	504	2.35	2.69	no
133	*L*	0.49	917	351	566	2.65	2.91	no
134	*L*	0.487	966	385	614	2.94	3.13	go
198	*L*	0.444	1050	432	675	3.92	4.14	no
199	*L*	0.444	1070	447	695	4.05	4.23	no
200	*L*	0.432	1215	552	845	5.27	5.22	go
201	*L*	0.4012	1391	671	994	7.28	7	go

[a]$S<45\ \mu$m; $L<150\ \mu$m.
[b]Go=complete reaction to Ti_5Si_3.

cal and SEM examination. Cross sections of reacted compacts show numerous voids indicative of contraction upon freezing of melted products. Shock pressure and energy were determined from the measured flyer velocity and initial powder porosity, and the Hugoniot properties for an unreacted elemental mixture as in Ref. 4. The equilibrium temperature for *unreacted* powder was calculated using the specific heats of Ti and Si, assuming all of the shock energy is converted to heat.[12] The recovered unreacted compacts exhibit negligible post-shock shear. Experimental and calculated parameters for each of the experiments are listed in Table I. The calculated equilibrium temperature and shock energy versus initial porosity, are presented in Fig. 2, in which reaction or no reaction is indicated for each particle size tested. While the number of experiments was insufficient to closely define the threshold values for initiation and completion of the reaction, it was sufficient to establish lower bounds (dashed lines) and upper bounds (solid lines) within about $\pm 10\%$.

A cross section of the larger particle compact with 0.49 initial porosity, and shock energy just below the threshold energy, was examined by SEM (calculated shock energy of 351 J/g, equilibrium temperature of 566 °C, and shock pressure of 2.65 GPa). Significant fracture is observed in the larger Si particles. Figure 3(a) shows dark (Si) and light (Ti) particles. Small areas of mixing and reaction at particle interfaces were observed between Si and Ti particles in widely separated regions. Most of them had the composition of $TiSi_2$ as determined by energy dispersive spectrometry. Figures 3(b) and 3(c) show regions of mixing and reaction. Propagation of the reaction appears to be by the production of a liquid phase product ($TiSi_2$) at the solid Ti liquid Si interface, the formation of spherical nodules of this product, and subsequent solidification as described by Meyers *et al.*[8] One of these regions appears to be a quenched liquid mixture of liquid Si and $TiSi_2$ [Fig. 3(c)]. Significant fracture is observed in the Si particles. The amount of $TiSi_2$ was insufficient to give observable peaks in an x-ray diffraction scan of this sample (below 5% volume fraction). The highest density of reaction regions was found between the flyer plate-powder

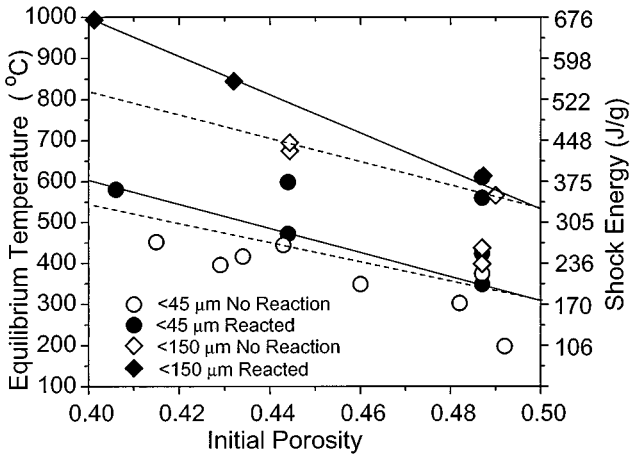
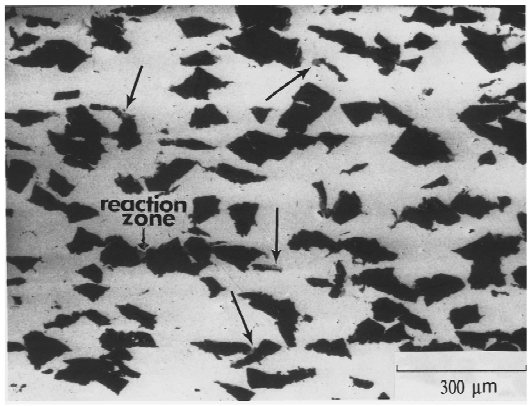
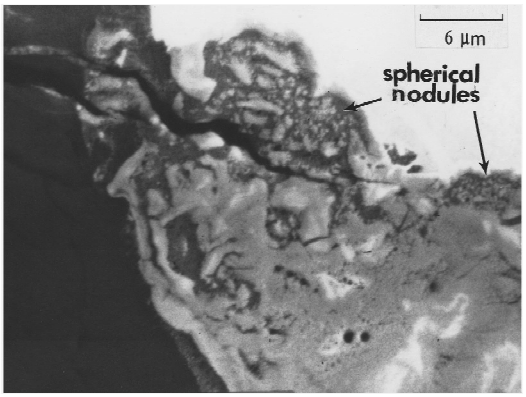


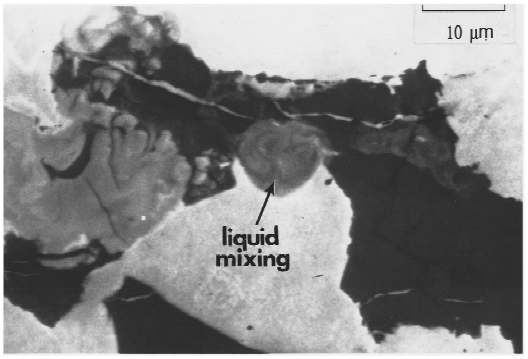
FIG. 2. Equilibrium temperature and shock energy vs initial porosity for two mixes of 5Ti+3Si (atomic ratio) powders. Dotted lines show approximate lower bounds for the reaction forming Ti_5Si_3 and solid lines show approximate upper bounds.



(a)



(b)



(c)

FIG. 3. Backscattered SEM micrographs of isolated regions of a cross section of the compact of the larger particles with an initial porosity of 0.49. Ti (light), Si (dark), and mixed areas are shown. The gray regions in (b) have the composition of $TiSi_2$ as identified by energy-dispersive x-ray. The gray region in (c) appears to show a quenched liquid mixture of Si and $TiSi_2$.

interface and the plane where the unloading wave from the back of the flyer catches the initial shock wave.

IV. DISCUSSION

Figure 2 shows the threshold shock energy increases with particle size and with decreasing porosity for the 5Ti +3Si powder mixtures. A description of the conditions for reaction initiation in shocked powders must take into account the dynamic processes which occur at the powder interfaces and within the powder interiors. Bordeaux and Yavari[13] gave two critical conditions for self-sustaining reactions in unshocked materials:

(a) the heat of mixing must be sufficiently in excess of the energy to form melt in the mixture and
(b) the mixing reaction time must be sufficiently shorter than the time required for dissipation of the heat of reaction to the surrounding material.

Condition (a) is met for the 5Ti+3Si mixes under adiabatic conditions when the shock energy at the threshold values is added to the heat of mixing (an extension of calculations for combustion synthesis of silicides made by Bhaduri *et al.*[14]). This is supported by the observation of voids in the recovered compacts which reacted. Condition (b) for the mixing time and the heat dissipation time from Ti and Si powder interfaces to surrounding powder, the flyer, and the steel target assembly and the validity of assuming near-adiabatic conditions requires careful consideration.

Powder-powder thermocouple measurements[12] show crush-up times of about 40 ns for Cu-constantan powders (<75 μm) during which the thermocouple emf rises to a peak value and decays to a particle equilibrium value with a time constant of 200–500 ns corresponding to the thermal relaxation for particles with a hot surface. The peak emf was on the order of 70% greater than the emf at equilibrium. The recorded emf values represent an average emf generated over the contact interface between the Cu and constantan powder layers (macroscopically a plane interface). Therefore the local peak temperatures are expected to be significantly in excess of the temperatures deduced from the emf measurements. Microstructural evidence of melting has been observed in a number of nonreacting shock compacted powders, typically in regions where voids collapsed on melt which flowed from deformation-heated surfaces.[7,8,15–17] Therefore it is questionable that shock-induced reactions in powders, where the equilibrium shock temperature is below the melting points of the reactants, necessarily indicates *solid-state* reaction as stated in Ref. 9.

The equilibrium temperatures just below the reaction thresholds in the present investigation are all below the melting points of Si and Ti, but *local* melting was very probable in regions where the porosity exceeded the average value. In widely separated regions where reactions started, as seen in Fig. 3 (shock energy just below the threshold), reaction was quenched by heat flow into the cooler particle interiors. The observation of spherules with the composition of $TiSi_2$ in Fig. 3(b) indicates molten $TiSi_2$ was ejected into liquid Si. This liquid state reaction mechanism under shock compression was first observed by Vecchio *et al.*[6,7]

The lower density of quenched reaction regions observed near the flyer-powder interface and near the plane of unloading of the initial shock wave, is attributed to heat loss to the cooler flyer plate and the cooler part of the compact, which was shocked to a much lower pressure (the pressure does not unload to zero, as the flyer plate was backed by a nylon sabot of relatively low shock impedance). It should be noted that the flyer plate interface was subjected to the maximum duration of high shock pressure, and the catch-up plane

to the minimum duration. As the shock energy is increased above the threshold value, the additional shock heating lowers the rate of heat loss to the particle interiors, and the reaction is not quenched. We presume the $TiSi_2$ reaction then proceeds, melting more Si and heating the adjacent Ti to its melting point. Under adiabatic conditions, Ti+2Si reacts with a resulting temperature which melts the $TiSi_2$. Since there is an excess of Ti even with complete reaction of the Si to $TiSi_2$, the liquid Ti and $TiSi_2$($7Ti+3TiSi_2$) reacts to Ti_5Si_3, which under adiabatic conditions results in a temperature which exceeds the melting point of Ti_5Si_3.[14]

Increases in the melting temperature of the reaction products with shock pressure could suppress melting and prevent the liquid-state mechanism for propagation of the reaction. This could be responsible for the high pressure effect observed by Boslough and Graham.[1] We attribute the increase in threshold shock energy with increasing particle size to:

(a) increase in volume per particle which acts as a heat sink for quenching the reaction, and leads to higher rates of cooling,
(b) decrease in specific area of reactants in contact.

Both of these effects are mitigated but not dominated by the increase of individual void volume in the larger particle powder mixes.

Quasi-static pressing of the powders prior to shock consolidation reduces the size of the pores where reaction is most likely to be initiated. The larger initial contact areas between particles in the powders with lower initial porosity will lead to less shear deformation in the shock crush-up process. These effects lead to an increase in shock energy threshold with a decrease in porosity.

The results of the present investigation lead to an alternative explanation for the ''shock activation'' reported by Deevi and Thadhani.[9] The powder which was produced from shocked but unreacted Ni+Si by grinding was found to have a lower DTA temperature threshold than the unshocked powder with the same porosity. It is very probable that the grinding of the shocked but unreacted powder produced particles of Si and Ni which were smaller than the unshocked powder particles, which could account for the reduced thermal energy threshold.

V. CONCLUSIONS

(1) Reaction initiation occurs at melt pools of Si formed in localized sites of excess initial porosity forming $TiSi_2$ with no evidence of *solid-state* reaction. The reaction propagates by the mechanism discussed by Vecchio *et al.*[6,7] and may be quenched by heat flow to the cooler particles interiors when the shock heating is below a threshold energy level. Above the threshold subsequent reaction of Ti and $TiSi_2$ forms Ti_5Si_3 and the heat liberated by the reaction melts the product.
(2) An increase in particle size of 5Ti+3Si powders increases the shock threshold energy for reaction. This is attributed to a decrease in the specific area of reactants in contact and an increase in heat sink volume per particle which leads to higher cooling rates at local hot spots.
(3) A decrease in initial porosity of the powders increases the threshold energy for reaction. This is attributed to a reduction of: (a) the volume of the larger pores which act as initiation sites, (b) the shear deformation produced by the shock, with a corresponding reduction in the specific area of reactants produced by the shock.
(4) Some conclusions from previous work on shock-induced reactions should be examined in the light of (1) and (2) above for shock activation as well as solid-state, rather than liquid–solid state reaction.
(5) Quantitative measurements of reaction rates, combined with time dependent analyses of shock heating, particle, and reactant melting from the heat released, and the heat thermally dissipated are needed to quantify and model the shock-induced reactions. This cannot be done for the recovery experiments, and wave velocity or optical temperature measurements made to date.

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